The Substituent Effects on π-type Pnicogen Bond Interaction

Jian-Qing Zhu[1], Sheng-Wei Cao[2], Wei Wang[3], Xiao-Lu Xu[4] and Hui-Ying Xu[4]*

[1] Department of Basic Courses, Zhejiang Shuren University, Hangzhou 310015, China
[2] ZhejiangLinix Motor CO., LTD, Dongyang 322118, China
[3] Zhejiang Surveying Institute of Estuary and Coast, Hangzhou 310008, China
[4] College of Biology & Environment Engineering,ZhejiangShuren University, Hangzhou 310015, China

xuhy65@163.com

Abstract. Intermolecular interactions between PH_2Cl and Ar-R（R=H, OH, NH_2, CH_3, Br, Cl, F, CN, NO_2）were calculated by using MP2/aug-cc-pVDZ quantum chemical method. It has been shown from our calculations that the aromatic rings with electron-withdrawing groups represent much weaker binding affinities than those with electron-donating groups. The charge-transfer interaction between PH_2Cl and Ar-R plays an important role in the formation of pnicogen bond complexes, as revealed by NBO analysis. The π-type halogen bond was also calculated and comparison of these two π-type interactions was made. It has been revealed that the π-type pnicogen bond systems are more stable than the halogen bond ones.

1. Introduction

Molecular interaction, closely correlated to various physicochemical properties, environmental governance and material structures and so on, has been of great concern in chemistry subject, environmental science, material science and some other fields[1-2]. The hydrogen bond interaction is of typical molecular interaction. Then, the halogen bond [3], lithium bond [4] and other weak interaction were found. In 2009, Hey-Hawkins, et al [5] proved the existence of P···P non-bond interaction via ^{13}C {^1H, ^{31}P} NMR experiment. Scheiner[6] theoretically calculated the geometrical structure and interaction energy of a series of pnicogen bonds systems including P···P and N···P, etc. Furthermore, the research on pnicogen bond interaction attracted the attention from theoretical and experimental chemists [7,8]. PH_3 is the simplest donor molecule in the pnicogen bond with a weak pnicogen bond interaction. When one of the H atoms is replaced by Cl atom (PH_2Cl), the P···N pnicogen bonds interaction formed between PH_2Cl and the representative electron donor NH_3 even exceeds the hydrogen bond interaction between water molecules [9], so PH_2Cl is often used as the donor model molecule in the research on pnicogen bond interaction [10]. In this paper, the interactions between PH_2Cl and the substituted benzene (Ar-R, R = H, OH, NH_2, CH_3, Br, Cl, F, CN, NO_2) are calculated by the quantum chemistry method, and to explore the geometrical structure, electronic structure and interaction energy of π-type pnicogen bond between PH_2Cl and the aromatic compound. Furthermore, the effect of the substituting group in the aromatic ring to the stability of π-type pnicogen bond complex are considered, in order to provide a theoretical basis for recognizing the nature of π-type pnicogen bonds, the application of the environmental governance and material structures.

2. Computational Methods

The structure optimizations and energy calculations of all molecules are performed by Gaussian 09[11] program package. In consideration of the importance of electron correlation for accurate interaction energy, the structure optimizations of all monomers and complexes are performed by MP2 method with aug-cc-pVDZ basis set, and no symmetry limit is applied to the optimization. References also show this method is applicable for the research on pnicogen bond interaction [12]. The interaction energy (ΔE_{int}), obtained from the complex energy deducting two monomer energies, is corrected to interaction energy (ΔE_{int}^{CP}) after the BSSE (Basis set superposition error) is corrected by CP (counterpoise)[13]. To further investigate the geometric and electronic properties of the complex systems, the second-order perturbation stabilization energy (ΔE^2) and the charge transfer quantity are calculated by the NBO program in the Gaussian 09 program package.

3. Results and Discussion

3.1. Geometrical structure and interaction energy

The stable structures of the complexes constructed between PH_2Cl and the substituted benzene (Ar-*R*, *R* = H, OH, NH_2) are obtained at level MP2/ aug-cc- pVDZ, and the geometrical structures are shown as figure 1. As can be seen from figure 1, the pnicogen bond interaction is generated between the P atom in PH_2Cl and the π-electron in the aromatic ring. According to our aforesaid definitions [14], the α angle is the included angle between the vector from the P atom to the hetero ring centroid and the vector at P-Cl bond direction (see figure 2), and the values of angle α for complexes **1~9** are shown in table 1. The angle α values in table 1 show that the angle α of 8 complexes is almost 180° except complex **3**, i.e. the three points of Cl, P, and the centroid are almost at the same straight line. The optimization result for complex **3** shows that one of the H atoms (H17) in PH_2Cl is also close to the aromatic ring center, i.e. a certain π-type hydrogen bond interaction is formed between the atom H in PH_2Cl and the π-electron in the aromatic ring, so the decreasing of angle α is caused by the interference of interaction P15-H17⋯⋯π.

Complex **1**   Complex **2**   Complex **3**
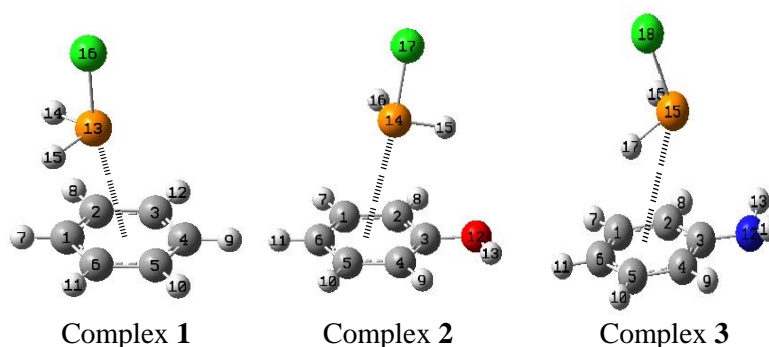
Figure 1. The optimized geometries of complexes**1-3** at MP2/ aug-cc-pVDZ level.
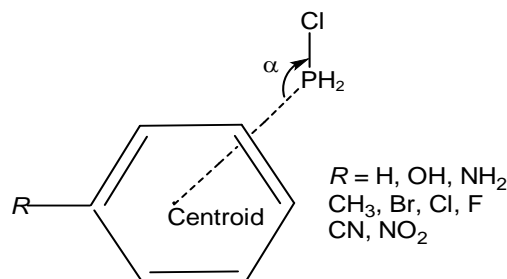
Figure 2. Geometric model of the pnicogen bonded angle α.

The uncorrected interaction energies (ΔE_{int}) and the corrected interaction energies ($\Delta E_{\text{int}}^{CP}$) of the complexes obtained at MP2/ aug-cc-pVDZ level are listed in table 1. Compared the ΔE_{int} with $\Delta E_{\text{int}}^{CP}$, it has been showed that the differences between the ΔE_{int} and $\Delta E_{\text{int}}^{CP}$ are 2.7 kcal·mol^{-1} to 3.5 kcal·mol^{-1}, so BSSE correction is necessary for the π-type pnicogen bond system. Complex **1** is the one formed by PH_2Cl and the non-substituted benzene, and which corrected interaction energy is -3.81 kcal·mol^{-1}. The corrected interaction energies of complex **2** and complex **3** are respectively -7.56 kcal·mol^{-1} and -9.65 kcal·mol^{-1}, which are much larger than the that of complex **1**. Because the substituted groups, -OH and -NH$_2$, are the electron donor groups , the electron density of π-electron system in the benzene ring is increased, the interaction between PH_2Cl and π-electron is stronger, and the interaction energy of the complex is larger and the complex is more stable. Similarly, the electron donating capacity of the group -CH$_3$ is weaker than the above two groups, so the interaction energy of complex **4** is smaller than that of complexes **2** and **3**. The corrected interaction energies of complexes **7~9** are respectively -3.55 kcal·mol^{-1}, -3.44 kcal·mol^{-1}, and -3.45 kcal·mol^{-1} which are smaller than the interaction energy of complex **1**, i.e. the complexes **7~9** are less stable than complex **1**. This is because the electron-withdrawing groups, -F、 -CN and -NO$_2$, reduce the π-electron density in the benzene ring, and result in the weakening of the interaction between P and π-electron. It is remarkable that the substituting groups -Br and -Cl in complex **5** and complex **6** are electron-withdrawing groups, but their interaction energies are a little larger than complex **1**. The reason may be the weak hydrogen bonds interaction between the hydrogen atom in PH_2Cl and halogen atom of the substituting group. It can be clearly seen in the geometrical structure of figure 1, and also proven by the following NBO analysis.

Table 1. The geometric parameters and interaction energies of complexes at MP2/aug-cc-pVDZ level[a]

Pnicogen bonding Complexes	ΔE_{int}	$\Delta E_{\text{int}}^{CP}$	α/(°)	Halogen bonding Complexes	ΔE_{XB}^{CP}
Complex **1** (H_2ClP····Ar-H)	-6.54	-3.81	169.1	PH_2Cl····Ar-H	-1.58
Complex **2** (H_2ClP····Ar-OH)	-10.66	-7.56	169.3	PH_2Cl····Ar-OH	-4.99
Complex **3** (H_2ClP····Ar-NH$_2$)	-13.09	-9.65	145.6	PH_2Cl····Ar-NH$_2$	-6.00
Complex **4** (H_2ClP····Ar-CH$_3$)	-7.19	-4.28	167.1	PH_2Cl····Ar-CH$_3$	-2.09
Complex **5** (H_2ClP····Ar-Br)	-7.57	-4.12	171.5	PH_2Cl····Ar-Br	-2.05
Complex **6** (H_2ClP····Ar-Cl)	-7.22	-4.05	170.1	PH_2Cl····Ar-Cl	-1.97
Complex **7** (H_2ClP····Ar-F)	-6.49	-3.55	171.8	PH_2Cl····Ar-F	-1.82
Complex **8** (H_2ClP····Ar-CN)	-6.43	-3.44	168.8	PH_2Cl····Ar-CN	-2.35
Complex **9** (H_2ClP····Ar-NO$_2$)	-6.63	-3.45	170.1	PH_2Cl····Ar-NO$_2$	-2.74

[a] interaction energies are given in kcal·mol^{-1}

The halogen bond is the interaction between the halogen atom and the electron donor in the halogenous molecule. It was found earlier than the pnicogen bond, and the research on halogen bonds is more mature than the pnicogen bond. In this research system, when the π-type pnicogen bond

interaction can be generated between the PH_2Cl molecule and the aromatic compound, a π-type halogen bond complex can be generated between π electron of the aromatic ring and atom Cl in the PH_2Cl molecule via the π-type halogen bond interaction. The molecular structures of nine typical halogen bond complexes are shown in Figure 3. As a comparison, their structures are optimized at MP2/aug-cc-pVDZ level, and then their corrected interaction energies (ΔE_{XB}^{CP}) which are corrected through the BSSE are shown in Table 1. Comparing the corrected interaction energy ΔE_{int}^{CP} of the pnicogen bond system and the corrected interaction energy (ΔE_{XB}^{CP}) of the corresponding halogen bond system, it has been found that the π-type pnicogen bond system is more stable than the π-type halogen bond system. It is caused by the unbalanced distribution of positive electrostatic potential in the PH_2Cl. As can be seen in Figure 3, in the same aromatic π electron donor, the positive electrostatic potential at the top of atom P is larger than that at the top of atom Cl.

PH₂Cl·····Ar-H   **PH₂Cl·····Ar-OH**   **monomers PH₂Cl**
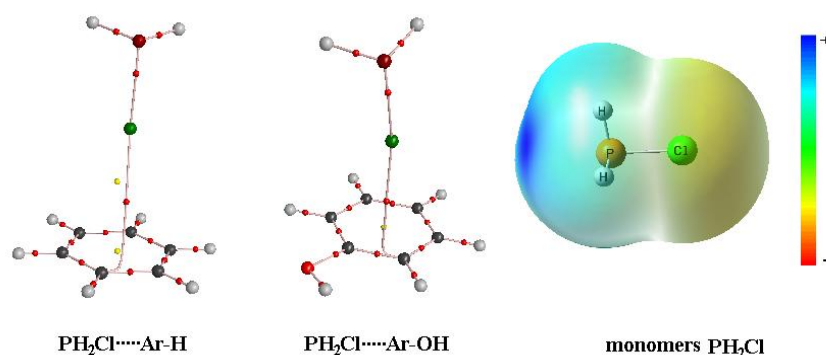
Figure 3. Molecular graph of PH_2Cl.....Ar-H and PH_2Cl.....Ar-OH, and electrostatic potential surface of monomers PH_2Cl.

3.2. NBO analysis

Table 2 shows the donor-acceptor orbital, the second-order perturbation stabilization energy (ΔE^2), and the charge transfer quantum (Q_{CT}) of 9 π-type pnicogen bond complexes at level MP2/aug-cc-pVTZ.

Table 2. Natural Bond Orbital Analysis of complexes **1-9** at the MP2/ aug-cc-pVDZ level

Complexes	Donor NBOs	Acceptor NBOs	ΔE^2/ kcal.mol^{-1}	Q_{CT}/ e
Complex **1** (H₂ClP·····Ar-H)	BD (2) C1-C6 BD (2) C2-C3	BD* (1) P13- Cl16	3.05 0.56	0.01115
Complex **2** (H₂ClP·····Ar-OH)	BD (2) C1-C6 BD (2) C2-C4	BD* (1) P14- Cl17	3.50 0.62	0.01536
Complex **3** (H₂ClP·····Ar-NH₂)	BD (2) C2-C3 BD (2) C1-C6	BD* (1) P15- Cl18 BD* (1) H17- P15	4.47 1.02	0.01614
Complex **4** (H₂ClP·····Ar-CH₃)	BD (2) C1-C6 BD (2) C2-C3	BD* (1) P16- Cl19	2.30 1.10	0.01007
Complex **5** (H₂ClP·····Ar-Br)	BD (2) C2-C3 Lp (3)Br	BD* (1) P13- Cl16 BD* (1) H14- P13	2.85 0.81	0.01250
Complex **6** (H₂ClP·····Ar-Cl)	BD (2) C2-C3 Lp (3)Cl	BD* (1) P13- Cl16 BD* (1) H14- P13	2.91 0.49	0.01179
Complex **7** (H₂ClP·····Ar-F)	BD (2) C2-C6 BD (2) C1-C6	BD* (1) P13- Cl16	3.06 0.43	0.01077

Complex **8** (H$_2$ClP$\cdots$Ar-CN)	BD (2) C6-C7	BD* (1) P1- Cl 4	2.78	0.00643
Complex **9** (H$_2$ClP$\cdots$Ar-NO$_2$)	BD (2) C5-C6 BD (2) C7-C8	BD* (1) P1- Cl 4	2.30 0.57	0.00953

The second-order perturbation stabilization energy (ΔE^2) can be obtained from the following equation (1):

$$\Delta E^2 = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\varepsilon_j - \varepsilon_i} \tag{1}$$

Where, q_i is the donor orbital occupancy, ε_i and ε_j are the diagonal elements (orbital energies), and F is the NBO Fock matrix element. It has been shown from the donor-acceptor orbital for complexes **1-9** in table 2, that the pnicogen bonds interaction is mainly the interaction between the C-C π bonding orbital and the σ anti-bonding orbital of P-Cl in the monomer PH$_2$Cl. The three complexes **3**, **5** and **6** are further involved with the hydrogen bonds interaction in addition to the pnicogen bond interaction. The second-order perturbation stabilization energy values indicate that the pnicogen bond interaction, followed by the hydrogen bond interaction, plays a key role in the complex stability. The existence of the supportive hydrogen bond interaction is the fact that the interaction energies of complexes **5** and **6** are higher than that of complex **1** in the above analysis, and why the angle α is smaller in the complex **3**.

The molecular interaction is always accompanied by charge transfer, and the charge transfer quantities in complexes **1-9** are shown in table 2. As can be seen in table 2, the charge quantities transferred from the aromatic compound to PH$_2$Cl molecule are from 6me to 16me. The charge quantity transferred is not so much, and it complies with the soft acid – soft alkali model (PH$_2$Cl molecule as the soft acid and the aromatic compound as the soft alkali). The plot of the charge transfer quantity and the corrected interaction energy is shown in Figure 4. The curvilinear equation (2) is as below:

$$\Delta E_{\text{int}}^{CP} = -11.215 + 1852.819\, Q_{CT} - 106824.298\, (Q_{CT})^2 \tag{2}$$

$$R = 0.954 \qquad SD = 0.540 \qquad N = 9$$

Figure 4 shows that the charge transfer quantities of the 9 complexes decrease with their interaction energies decreasing, and this result indicates that the charge transfer plays an important role in the complex stability.
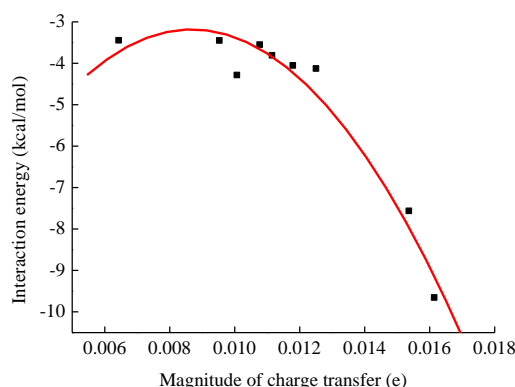
Figure 4. The relationship between charge transfer and interaction energy.

4. Conclusion

The geometrical structural optimization, energy calculation and topological and graphic analyses for the various pnicogen bond system of PH_2Cl and Ar-*R* (*R*=H, OH, NH_2, CH_3, Br, Cl, F, CN, NO_2) have been made at level MP2/ aug-cc-pVDZ. The results have showed, the complex pnicogen bond interaction will be strengthened when the substituting group in the benzene ring is the electron donating group, and the complex pnicogen bond interaction will be weakened when the substituting group is the electron withdrawing group. To compare the interaction energy of the π-type pnicogen bond system with the halogen bonds system, the interaction energy of π-type halogen bond system is also calculated, and it is showed that the π-type pnicogen bond system is more stable. NBO theory is used to analyze the correlation between the second-order perturbation stabilization energy, the charge transfer quantum and the interaction energy, and the result shows that the charge transfer plays an important role in the stability of the pnicogen bond complex.

5. Acknowledgments

6. References

[1] Gillet N, Chaudret R, Contreras-Garc á J, Yang W, Silvi B and Piquemal J 2012 *J. Chem. Theory Comput*. **8**, 3993
[2] Mahadevi A S and Sastry G N 2013 *Chem. Rev.* **113**, 2100
[3] Wash P L, Ma S, Obst U and Rebek J J 1999 *J. Am. Chem. Soc.* **121**, 7973
[4] Ault B S 1978 *J. Am. Chem. Soc.* **100**, 2426
[5] Bauer S, Tschirschwitz S, Lönnecke P, Frank R, Kirchner B, Clarke M L and Hey-Hawkins E 2009 *Eur. J. Inorg. Chem.* 2776.
[6] Scheiner S 2011 *J. Chem. Phys.* **134**, 164313
[7] Del Bene J E, Alkorta I, Sánchez-Sanz G and Elguero J 2012 *Chem. Phys. Lett.* **538**, 14
[8] Alkorta I, Sánchez-Sanz G, Elguero J and Del Bene J E 2013 *J. Phys. Chem. A* **117**, 183
[9] Scheiner S 2011 *J. Phys. Chem. A* **115**, 11202
[10] Adhikari U and Scheiner S 2012 *Chem. Phys. Lett.* **532**, 31
[11] Frisch M J 2009 *Gaussian 09 (Revision A.01)*, Gaussian, Inc., Wallingford CT
[12] Adhikari U and Scheiner S, 2012 *Chem. Phys. Lett.* **536**, 30
[13] Boys S F and Bernardi F, 1970 *Mol. Phys.* **19**,553
[14] Xu H Y, Wang W and Zou J W 2013 *Acta Chim. Sinica* **71**, 1175